

As(V) SORPTION ON HEMATITE: COMPLEXATION GEOMETRY OBTAINED FROM COMBINED SURFACE X-RAY DIFFRACTION AND GRAZING-INCIDENCE X-RAY ABSORPTION SPECTROSCOPY

Glenn Waychunas, Tom Trainor¹, Peter Eng², James Davis³, and John Bargar⁴

¹University of Alaska, Fairbanks, ²University of Chicago

³U.S. Geological Survey, Menlo Park, ⁴Stanford Synchrotron Radiation Laboratory

Contact: Glenn Waychunas, 510/495-2224. GAWaychunas@lbl.gov

RESEARCH OBJECTIVES

The objectives of this work were to combine surface x-ray diffraction results of wet hematite surfaces, with arsenate complexation structure derived from surface extended x-ray absorption fine structure (EXAFS) measurements. Using these two techniques together, it is now possible to describe the geometry of sorbed metal complexes with unrivaled detail. This enables testing of both structural and thermodynamic models for sorption and surface complexation, and direct comparisons with molecular-dynamics (MD) simulations of surface reactions.

APPROACH

Surface diffraction of the wet hematite (0001) and (1-102) surfaces can be done using crystal truncation rod (CTR) measurements to obtain the reconstructed or relaxed configuration of surface ions. This has been done (Trainor et al., 2005) and shows that the wet hematite surface is highly defective, with iron atoms missing from the double layers that characterize the bulk structure. The missing atoms are those that would ordinarily share FeO₆ polyhedral faces with one another. We then obtained polarized EXAFS structure functions for arsenate sorbed on the wet (0001) and (1-102) hematite surfaces at SSRL beamline 11-2, and used the hematite surface structure to interpret the results.

ACCOMPLISHMENTS

The results show details of surface complexation that could not have been recovered without these methods (Figure 1). In particular, there is an abundance of "edge-sharing" arsenate-FeO₆ units on the surface, which results from the high proportion of available edge-sharing sites, but relative scarcity of adjacent FeO₆ units allowing "corner-sharing" arsenate attachment. The measurements also

demonstrated self-consistency of the hematite surface structure model, and thus helped to verify the CTR diffraction work. We also determined that the method could be applied to complexation coverages as low as about 5% of one monolayer.

SIGNIFICANCE OF FINDINGS

The results indicate the powerful nature of such combined surface probes of interfacial reactions. Prior to this type of study, the surface structure information would not have been accurate enough to derive a proper model of the complexation. We can now proceed to develop MD simulations of surface reactions with a detailed knowledge of the expected complexation geometries. This work is continuing with other surface

sorbants, including silicate, phosphate, and selenate, and the CTR work is being extended to include refinements with sorbates present on the scattering surfaces.

RELATED PUBLICATIONS

Trainor, T., P. Eng, G.E. Brown, G. Waychunas, M. Newville, S. Sutton, and M. Rivers, Structure and reactivity of the hydrated hematite (0001) surface. *Surface Science*, 573, 204-224, 2005.

Waychunas, G.A., T. Trainor, P. Eng, J. Catalano, G.E. Brown, J. Rogers, and J. Bargar, Surface complexation studied via combined grazing-incidence EXAFS and surface diffraction: Arsenate on hematite. *Anal. Bioanal. Chem.* (in press), 2005.

ACKNOWLEDGMENTS

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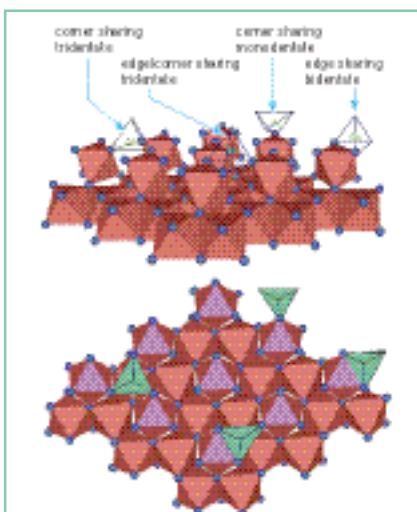


Figure 1. Cartoon showing two views of arsenate complexes (green tetrahedral) as they could sorb on a wet hematite (0001) surface. Of these types, only the edge-sharing bidentate complex is actually observed. Note that the hematite surface is only partially populated by FeO₆ unit (red octahedral) as indicated by CTR work.